BODY OF PROPOSAL

A) Description of Experiment (including need for synchrotron radiation):

I. Introduction

The electronic and magnetic properties in *f*-electron intermetallic systems are mainly driven by interactions between the *f* and *d*-electrons that are close to the Fermi energy. Depending on the *f-d* hybridization strength, these systems typically can have either an antiferromagnetic (AF) ground state (i.e. the Ruderman-Kittel-Kasuya-Yosida, or RKKY, interaction dominates) or a nonmagnetic ground state where *f* and *d* spins are anti-aligned *locally* (i.e. the Kondo effect dominates). In these situations, the electronic and magnetic properties are described well as a collection of non-interacting quasiparticles, that is, screened electron clouds with enhanced mass. This concept was brought forward by Landau and is known as "Fermi liquid theory" (FLT).[1] Some notable physicists have called the success of FLT one of the great triumphs of 20th century physics: FLT allows one to solve for the interactions between ~10^{23} particles without the need for solving 10^{23} coupled equations, and describes a very wide range of systems. By using FLT and determining certain parameters, most magnetic and electronic properties can be calculated in many systems and related to each other. Recently, however, there has been mounting interest in so-called "non-Fermi liquid" (NFL) systems,[2] where atypical electronic and magnetic properties have been measured. The most famous NFL systems are the high-T_C superconductors, which have linear resistivities with temperature above T_C.[3]

There are many competing theories of NFL behavior. Early examples include multichannel Kondo theories[4] and those based on the idea of a quantum critical point (QCP),[5] that is, a critical point between RKKY and Kondo ground states at zero temperature. As such, many researchers believe that NFL behavior can be generated in a well-ordered crystalline material. This notion poses a problem because many of the materials exhibiting NFL behavior are known to be disordered. Some researchers have therefore been exploring models where disorder is a necessary component. These theories include Kondo disorder,[6] where a distribution of *f-d* interaction strengths creates NFL behavior with essentially no new physics, and QCP models with the addition of lattice disorder which creates a larger region in phase space for the critical point ("Griffiths' phase").[7] Therefore, the notion of a disordered lattice is a central dividing line between the various theories.

Consider the case of $UCu_{5-x}Pd_x$, whose phase diagram[8] is shown in Fig. 1. For a general discussion, we could take the *x*-axis to either be pressure or disorder. If it were pressure, then as we increase pressure, one way to describe the physics is in terms of an increased *f-d* hybridization, which lowers the strength of the RKKY interaction and therefore the Néel temperature. When this transition temperature reaches zero, we would be near a quantum critical point at low temperatures, and the system would enter a NFL region. As the pressure increases further, the lattice may become unstable, and some kind of Fermi liquid could re-emerge (such as a heavy fermion, or even an AF or a spin-glass). Conversely, if the *x*-axis represents disorder, the increasing disorder could create regions of increased hybridization, destroying the long-range RKKY interaction, thus lowering T_N until the system is composed of many small domains that are only governed by Kondo physics. The distribution of hybridization strengths could create the distribution of Kondo temperatures, which would then explain the NFL behavior. Eventually, as the disorder is increased further, a spin glass (SG) phase develops. Another possibility is that the disorder and QCP concepts work together to create the NFL region, as in a Griffiths' phases. The SG phase would develop because the system is too far from the QCP for NFL behavior to exist.

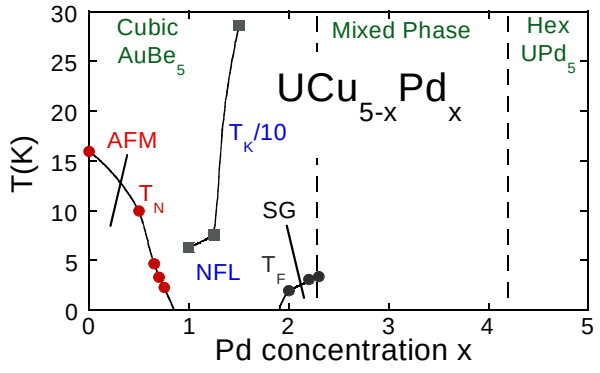

Figure 1. Phase diagram of $UCu_{5-x}Pd_x$. This diagram is in some ways generic to the non-Fermi liquid problem in *f*-electron systems, in that as the hybridization between *f* and conduction electrons is increased either by chemical pressure (as shown) or by real pressure, T_N is decreased to 0 K, beyond which a NFL regime develops.

Although we discuss $UCu_{5-x}Pd_x$ as a canonical example, many systems behave in a similar manner, either with similar phase diagrams or by exhibiting the behavior that defines part of this phase diagram. We propose to continue researching the important role that lattice disorder is playing in these kinds of systems. Our work is

expanding to include interesting materials from all parts of the generic phase diagram, including spin glass systems such as the pyrochlore $Y_2Mo_2O_7$ and URh_2Ge_2, as well as $UCu_{2.8}Pd_{2.2}$, and NFL systems such as UCu_4Pd, $U_3Ni_3Sn_4$, and $CeCu_2Si_2$. Moreover, we plan to continue our studies of the Kondo lattice systems for their own sake and as a control group for the NFL studies, with continuing studies on $YbCu_{5-x}Ag_x$ and others.

In the next section, we will summarize the results and measurements from the proposal that this proposal is renewing (#2545). We will then discuss the physical issues and materials that we will explore. We include a short discussion of our sample preparation and characterization capabilities, and then finish with some concluding remarks.

II. Previous progress from proposal 2545

The present proposal is meant as an extension to proposal 2545, and as such, we include a very brief summary of the data collection and manuscript status from that proposal. Many useful data sets were collected, although (to date) not all that were desired. The following point-by-point summary is only meant to demonstrate the success of the previous proposal. Please see the Activity Reports for details. The collected data includes:

1. A survey set of XAFS data were collected from all three elements in $UCu_{5-x}Pd_x$ and $UCu_{5-x}Pt_x$ ($x \approx 0$, 0.7 1.0 1.5 2.2, and 5). An Activity Report and a manuscript are in preparation. This study extends our initial work on UCu_4Pd,[9] which was the first to identify site interchange between Pd and Cu atoms in this system.
2. A survey set of XAFS data from the *M* edges in Yb*M*Cu_4 (*M* = Ag, Au, Cd, and Tl) was collected. No evidence of site interchange was found, and a manuscript is in preparation. High temperature XANES data from the Yb L_3 edge were also collected, but we suspect the samples oxidized. We are about to obtain an improved cryostat capable of at least 450 K (possibly 700 K) in which we can repeat these high temperature measurements in a better-controlled atmosphere.
3. XAFS data on the hexaborides SrB_6, LaB_6, GdB_6 and EuB_6 were collected as a function of temperature. An Activity Report and a manuscript are in preparation for the LaB_6 and EuB_6 data. The LaB_6 data will be presented in conjunction with neutron powder diffraction data. The EuB_6 data was collected at several temperatures around the ferromagnetic transition at 15 K. We determined that the lattice involvement is orders of magnitude less than in the colossal magnetoresistance perovskites. These results lay the groundwork for continuing studies on the hexaborides, especially the heavy fermion $La_{1-x}Ce_xB_6$ and $Sr_{1-x}Sm_xB_6$.
4. XAFS data on the spin glass $Y_2Mo_2O_7$ were collected. A manuscript has been submitted[10] which is the first to report structural disorder in the Mo sublattice. Many researchers believe such disorder is a necessary ingredient for the spin glass transition to occur in this compound. An Activity Report is in preparation.

Although a wide range of data were collected under prop. 2545, some of the global issues regarding a *changing* charge-spin-lattice interaction (as discussed in that proposal) cannot yet be discussed because some important compounds for that discussion have yet to be measured. These include $Sr_{1-x}Sm_xB_6$, and possibly EuSe and EuO.

III. Issues and Materials

Using a "typical" phase diagram as shown in Fig. 1 as a guide, we will focus on three classes of systems: spin glasses, Kondo lattices, and non-Fermi liquids. Although not stressed below, the reviewer should note that all of the proposed materials fall into three distinct crystal structure classes: the related $ThCr_2Si_2$ (I4/*mmm*) and $CaBe_2Ge_2$ (P4/*nmm*) structures (including URh_2Ge_2, $CeCu_2Si_2$, etc.), the hexaborides and the *C*15b structures (such as $YbAgCu_4$ and UCu_4Pd). The only outlier from this distribution is $U_3Ni_3Sn_4$, which has the $Y_3Au_3Sb_4$ structure.

A. Spin glasses

Spin glasses are an integral part of the phase diagram in Fig. 1, and are a direct consequence of disorder in magnetic systems.[11] This latter property is strongly related to the Kondo disorder model in the non-Fermi liquids (at least in mechanism), and so a clear understanding of the role of disorder in *f*-electron spin glasses is an essential building block. Moreover, some non-*f*-electron spin glasses are included in our studies to form a broader foundation.

Some spin glass systems that possess a high degree of geometrical frustration[12] have been identified recently that are apparently only weakly disordered from a structural point of view. Perhaps the best studied of these systems is the pyrochlore $Y_2Mo_2O_7$. Neutron diffraction studies indicated a lack of positional disorder in $Y_2Mo_2O_7$.[13] Our recent

XAFS results, on the other hand, discovered an unusual local distortion of the Mo-Mo pairs, whereby static (positional) disorder exists, but in a relatively small amount, and also only in directions that are perpendicular to the Y-Mo pairs.[10] This result is contrary to our previous measurement of isostructural $Tl_2Mn_2O_7$ and $Er_2Mn_2O_7$.[14] Although this measurement should help researchers understand the spin glass transition in $Y_2Mo_2O_7$ better, it raises the valid question of why $Y_2Mo_2O_7$ has a local distortion and other members of the pyrochlore series do not. One distinct possibility is that 6*s* electrons are in the conducting band in the Er and Tl pyrochlores, and that the known hybridization of the 6*s*/3*d*(Mn) bands in these systems somehow translates into an ordered Mn sublattice. Another possibility rests on ionic radii arguments for the *A* site. Neither of these arguments is particularly compelling, and so we will endeavor to do a more complete survey of the local structure properties of several pyrochlores, many of which have their own unique electronic and/or magnetic properties. Our future measurements will include the spin-ice system $Ho_2Ti_2O_7$, the spin glass $Tb_2Mo_2O_7$, the ferromagnet $Y_2Mn_2O_7$, and others.

While studies of the pyrochlore systems continue, we will also address the issue of U-based spin glasses. Our studies will focus initially on the URh_2Ge_2 intermetallic system. This system is similar to the pyrochlore spin glasses in that the initial measurements could not identify lattice disorder using neutron and x-ray diffraction, although an annealing study found that an AF transition could be obtained by changing properties of the heat treatment.[15] Ongoing annealing and crystallography studies have found structural differences between AF and SG samples, although the exact crystal structures of these materials is still not certain. Our initial XAFS measurements on these materials are consistent with a particular mix of phases (specifically a mix of the I4/*mmm* and the P4/*nmm* space groups) by observations from the Rh and Ge edges. We require much higher quality U edge data than what was previously obtained, and therefore plan to continue these studies.

Once these investigations are nearly completed, we will attack the SG part of the phase diagram in Fig. 1. As mentioned above, we have collected a survey data set on $UCu_{5-x}Pd_x$. A study of the SG part of the phase diagram will require a more focused set of data around the critical x=2.2 concentration. Moreover, our preliminary data suggest that the problem may be too difficult for Rietveld analysis and XAFS alone, and so we may elect to collect pair-distribution function (PDF) data on these materials as well.[16]

B. Kondo lattice

The "familiar" version of the Kondo effect is that of a magnetic impurity embedded in a nonmagnetic matrix, such as Cu:*Fe*. In this situation, one may ignore the long range effects of Fe *d*-band overlap between neighboring Fe's, and therefore of collective phenomena. As discussed above, the NFL behavior considered here is related to Kondo physics in one form or another, either via disorder, quantum critical points or both. The attempts to understand the role of disorder in such systems has necessarily caused researchers to focus on systems where the magnetic ion is actually part of a crystalline matrix, and therefore is part of the lattice where coherence (band overlap) effects can play a role. These systems are often referred to as "Kondo lattice" systems, because much of the physics of the Kondo effect is retained even in the presence of coherence effects as explained by Fermi liquid theory. However, the detailed understanding of the Kondo lattice is far from solved, although theoretical and experimental progress is being made.[17] If we are to understand the role of lattice disorder in the phase diagrams represented in Fig. 1, we must therefore continue to make progress understanding the "control" systems that are Kondo lattices.

Our work on measuring the Yb valence in the Yb*M*Cu_4 series demonstrates the failure of the single-impurity model (SIM) for tying together the magnetic susceptibility measurements with the valence measurements.[18] Initially, we could ascribe this failure to several possible mechanisms, including crystal field splitting and *M*/Cu site interchange. Our recent measurement at IPNS have virtually ruled out the possible crystal field splitting, and X-edge XAFS measurements have ruled out *M*/Cu site interchange for *M*=Ag, Au, Cd, and Tl. With no other possible mechanisms to cause the disagreements between the SIM and the data, we can now attempt to describe the real differences between the Kondo lattice and the SIM. Presently, we are comparing the results of measurements of the magnetic susceptibility $\chi(T)$, specific heat coefficient $\gamma(T)=C(T)/T$ and 4*f* occupation number $n_f(T)$ for the intermediate valence compounds Yb*M*Cu_4 (*M* = Ag, Cd, In, Mg, Tl, Zn) to the predictions of the Anderson impurity model, calculated in the non-crossing approximation (NCA). The crossover from the low temperature Fermi liquid state to the high temperature local moment state is substantially slower in the compounds than in the predictions of the NCA; this corresponds to the "protracted screening" recently predicted for the Anderson Lattice. We intend to extend these studies to higher temperature and to other Kondo lattice systems, such as CeB_6, $YbCu_5$ (which has only been recently made in the pure cubic form) and the $YbCu_{5-x}Ag_x$ series.

C. Non-Fermi liquids

Our first attempts to measure the presence of lattice disorder in an "ordered" NFL material were very successful: UCu_4Pd has significant site interchange between the Cu and Pd sublattices, which can produce a distribution of Kondo temperatures, and therefore, possibly NFL behavior. Our most recent results suggest that although the site interchange exists, it does not induce the extra lattice disorder that is required for the Kondo disorder model to work by itself. These measurements and analyses are still ongoing. However, it is now time to broaden the survey of NFL materials some more. Ideally, we will measure an NFL material that is nominally well ordered, one where some disorder is known to exist, and a system where the situation is still unclear. We have currently chosen the $U_3Ni_3Sn_4$, $CeRhRuSi_2$ and a material with the "ultimate" NFL behavior: the heavy-fermion superconductor $CeCu_2Si_2$.

$U_3Ni_3Sn_4$ is unusual even for an NFL material. Even though, generally speaking, polycrystals are thought to possess more and different kinds of disorder than single crystals, polycrystals of $U_3Ni_3Sn_4$ exhibit Fermi liquid behavior[19] while single crystals display a characteristic NFL magnetic susceptibility $\chi \propto T$-0.3 between 1.7 and 10 K. Moreover, the slightly off-stoichiometric $U_{2.9}Ni_3Sn_{3.9}$ has an electronic specific heat coefficient of $\gamma(T)$ that varies as $T^{1/2}$.[20] This behavior is contrary to the usual NFL behavior $\gamma(T) \propto \log(T)$, although similar behavior has been observed in $CeCu_2Si_2$ and $CeNi_2Ge_2$.[21] In fact a renormalization group calculation for magnetic fluctuations near an AF quantum critical point predicts such behavior.[5] Moreover, x-ray diffraction studies indicate the $U_3Ni_3Sn_4$ system is very well ordered, and excellent fits are obtained for the off-stoichiometric sample as well. Therefore, this system behaves oppositely to most other NFL materials: it appears that the more ordered systems have a tendency towards NFL behavior, and small changes in stoichiometry (likely too small for Kondo disorder to play a role) create even more unusual behavior. Obviously, the local structure of such a system should be measured very carefully.

As initially discussed above, a QCP can be accessed either by apply real pressure or by applying "chemical pressure" by disordering the lattice. The $CeRh_{2-x}Ru_xSi_2$ is a good system to consider the different approaches.[22] $CeRh_2Si_2$ has an AF transition at 35 K at ambient pressure, which can be reduced to 0 K under about 9 kbar. Substitution of Ru can produce a similar effect with $x \sim 0.95$. However, the linear coefficient to the specific heat does not diverge in $CeRh_2Si_2$ above 9 kbar, i.e., the system remains a Fermi liquid with a non-zero Kondo temperature. $CeRhRuSi_2$, on the other hand, has the typical logarithmically diverging $\gamma(T)$ of an NFL material. Calculations show that these data fit a Kondo disorder model well, although a crossover to Fermi liquid behavior at low temperatures is still poorly understood.[23] This system appears to be the strongest candidate for a pure Kondo disorder model, and therefore an ideal testing ground for some of the ideas and concepts we developed in our study of $UCu_{5-x}Pd_x$.

The compound $CeCu_2Si_2$ is one of a small number of heavy fermion compounds that are superconductors. For $CeCu_{2+x}Si_2$ superconductivity only occurs for $0.02<x<0.2$ while for $-0.1<x<0$ the samples are normal.[24] For $CeCu_{2+x}Si_2$ it is known that the superconducting samples have smaller cell volumes than the normal samples; but the difference between the structures for the two cases is unknown. To determine this difference, we performed[25] neutron diffraction on polycrystalline samples of non-superconducting $CeCu_{1.9}Si_2$ and superconducting $CeCu_{2.3}Si_2$. Using Rietveld refinement, we showed that both compounds could be well-fit assuming perfectly ordered and stoichiometric $CeCu_2Si_2$, but for the $CeCu_{2.3}Si_2$ sample, additional reflections occurred which could be fit assuming segregation of the appropriate amount of *fcc*-Cu. We were unable to detect any difference in the structure of the $CeCu_2Si_2$ phase between the superconducting and non-superconducting samples. Once again we have a case where disorder seems to be playing a role ($x \neq 0$ for superconducting samples), yet the average structure indicated by diffraction does not detect it. Indeed, some recent pair-distribution function analysis of neutron diffraction data has observed some subtle differences in the mean bond lengths in the superconducting material. XAFS analysis should help clarify this situation. These measurements can look for overall disorder around the magnetic (Ce) ion site, as well as look for Cu/Si site interchange in a similar manner to the analysis on URh_2Ge_2. Moreover, we can consider the *fcc* Cu to check that the diffraction analysis has a consistent phase fraction of $CeCu_2Si_2$. This experiment is likely going to be the most challenging of those proposed here.

Other related materials may be considered, such as $YbCo_2Ge_2$, $CeNi_2Ge_2$, $Y_{1-x}UPd_3$, $CeCu_6$, etc.

D. Overall sample characterization

Several collaborators will prepare samples. NFL materials will come from Prof. Maple, Prof. De Long, and Dr. Sarrao. Hexaboride samples are prepared by Prof. Fisk's group. Spin glass samples are prepared by Dr. Gardner and

Prof. Mydosh. Kondo lattice materials are prepared by Dr. Sarrao. We point out that many of these sample makers are leaders in their respective fields, and so our samples are among the most carefully prepared and characterized sample available. The XAS effort is tightly coordinated with the sample preparation effort, and therefore we hope to track changes in the electronic properties of samples with nominally the same composition to changes in the XAS properties. Other more extensive probes can also be deployed when appropriate, such as neutron PDF techniques.[16]

IV. Concluding Remarks

The scientific issues we cover in this proposal are fairly numerous, however, they focus around the central theme of understanding the interplay between the Kondo and RKKY interactions and their relation to lattice disorder. By varying the degree of these three interactions, a wide range of electronic behavior ensues, including AF, SG, FM, Kondo lattice, HF, NFL, etc. This proposal represents an attempt to understand the relationship between all these kinds of behavior by considering the three mechanisms responsible.

B) SSRL Experimental Equipment Required: Ionization detectors and sample positioners are required.

D) Previous Experience with the Technique and the Facility: Several investigators on this proposal have extensive experience running XAFS experiments at SSRL. Corwin Booth has experimented at SSRL since 1992 and has recently become a staff scientist in the Glenn T. Seaborg Center at LBNL. He has produced over 35 publications related to work done at SSRL. George Kwei has experience at SSRL dating back to the late 1980's doing XAFS experiments, and has recently performed x-ray diffraction and absorption studies. Jon Lawrence has been doing edge studies since 1996. J. Sarrao, Z. Fisk, J. Mydosh, M. B. Maple and L. De Long have no experience running at SSRL. They provide scientific and sample expertise, and may not be present for synchrotron data collection.

E) Safety Concerns: Many sample contain depleted uranium. Please see proposal form for details.

F) End Station and Beam Time Requirements: BL 4-3 (or equivalent) is generally required since many of the edges of interest are in the 20 keV range. 4-1 can work, but is very cramped with our cryostat and storage dewar. BL 2-3 can be utilized occasionally. 15 shifts twice a year should be a sufficient amount of beam time.

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